CO2 Reduction and Upgrading for e-Fuels Consortium

U.S. DEPARTMENT OF ENERGY

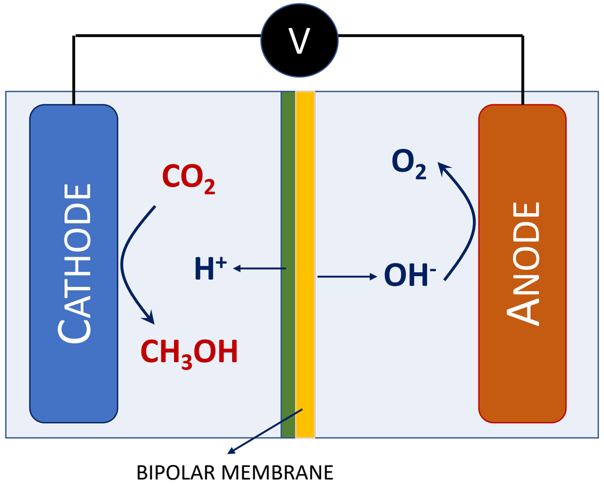
Electrode and Membrane Materials for CO_2 Electrolyzers: A Molecular Approach

WBS: 2.3.4.304/2.3.4.305

Apr 6 2023

Ksenia Glusac, ANL

Project Overview: Summary



Electrochemical CO_2 to CH_3OH conversion:

$CO_2 + H_2O \rightarrow CH_3OH + O_2$

-Catalysts for selective CO_2 reduction to CH_3OH

-Bipolar membranes for desired pH and prevention of CH_3OH crossover.

-Molecular approach: chemically tunable.

Funding:
DOE/EERE/Bioenergy Technologies Office

Performance Dates:
Jan 1, 2022 – Sep 30, 2024

TRL: 2-4

Participants

Glusac/ANL&UIC

Myers/ANL

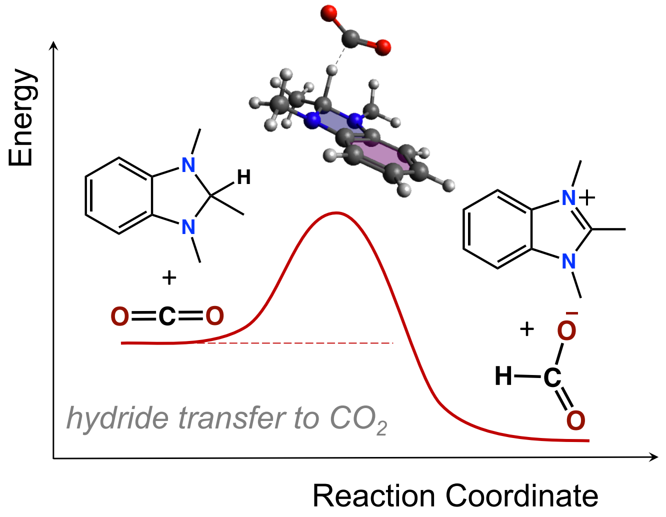
Smith/NREL&CU

Zapol/ANL

Project Overview: Glusac Group Expertise

Molecular bioinspired electrocatalysis/photocatalysis

NADH analogs: CO_2-to-formate

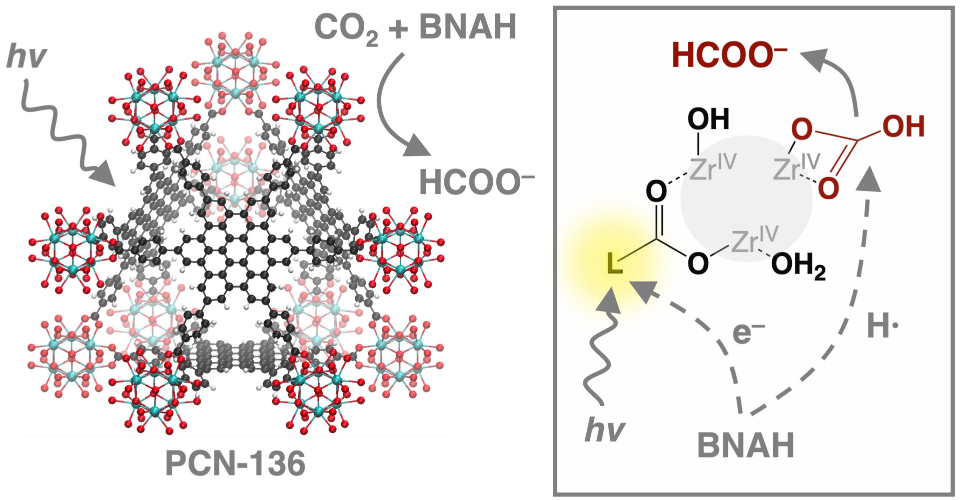


Accs Chem Res 2022

J Am Chem Soc 2019

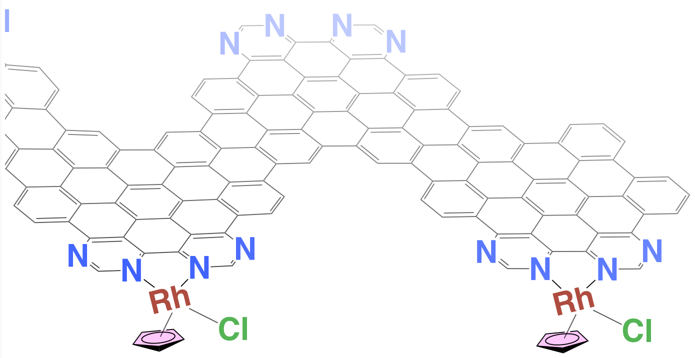
J Am Chem Soc 2018

Photoreactive CO_2 capture



ChemRxiv 2022; ChemRxiv 2023

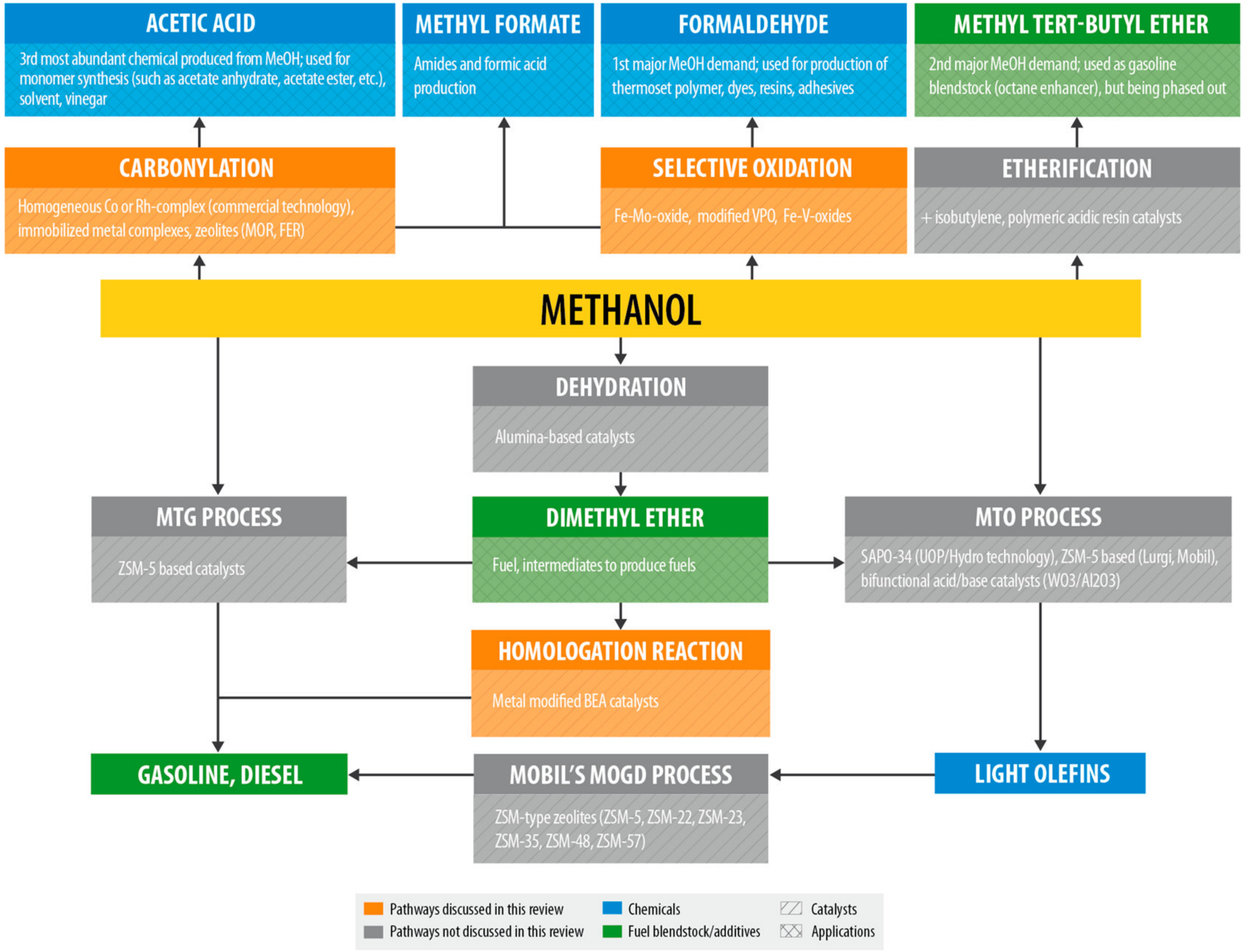
Molecule/Electrode Hybrid Catalysts



Nat Commun 2021

ACS Appl Electron Mater 2021

Project Overview: Methanol as fuel and chemical



Gary Grim, ACS Catalysis 2019, 4145

Project Overview: Thermal vs e-Methanol

Thermal Methanol:

Fuel Gas
Steam(H_2O)
Natural Gas
Reformer
Natural Gas(fuel)
Synthesis gas
$CO+H_2$
CO_2+H_2
Methanol Converter
H_2 Purge
To Burners
To H_2 consumers
Methanol/Water
CH_3OH/H_2O
Distillation
Methanol
Water


Methanol convertor


Reformer


Distillation tower

Non-renewable

2nd law of TD

No CO_2 removal

Project Overview: Thermal vs e-Methanol

e-METHANOL: **Existing plants use a 2-step process**

$$3H_2O \xrightarrow{\text{e-chem}} 3H_2 + 3/2O_2 \qquad CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O$$

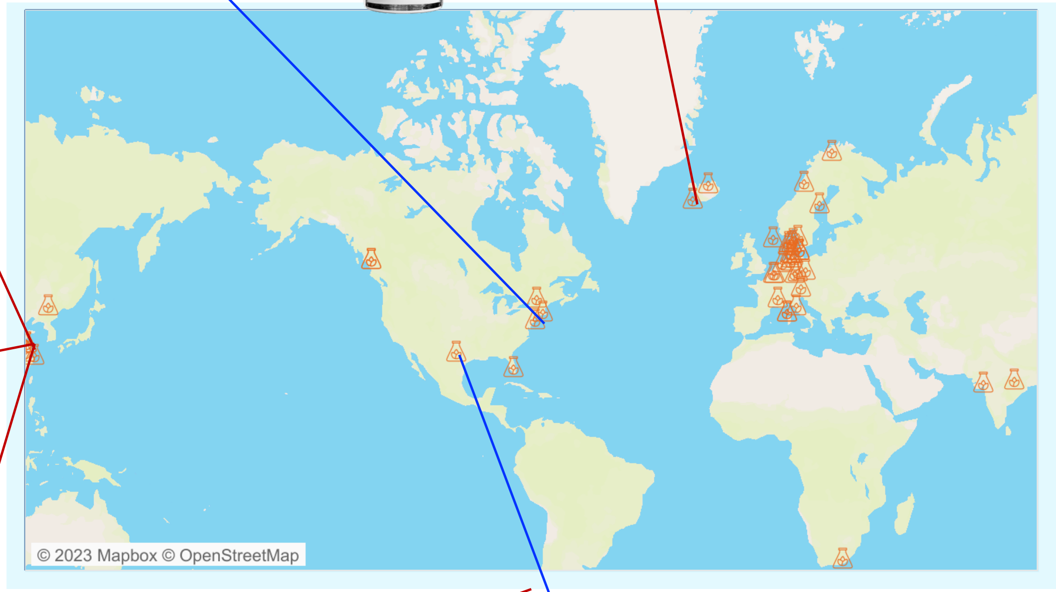
E-METHANOL PROJECTS IN THE WORLD:

Company: **Henan/CRI, China**
Capacity: **110 Kt/y**
CO_2 source: capture
Year: **2022**

Company: **Air Company, USA**
Capacity: **0.4 Kt/y**
CO_2 source: **biogenic**
Year: **2020**

Company: **CRI, Iceland**
Capacity: **4 Kt/y**
CO_2 source: **geothermal**
Year: **2011**

CARBON RECYCLING INTERNATIONAL



Company: **DICP, China**
Capacity: **1 Kt/y**
CO_2 source: N/A
Year: **2020**

Company: **Blue Chemical, China**
Capacity: **5 Kt/y**
CO_2 source: N/A
Year: **2020**

Company: **Siemens, Porshe, HIF, Chile**
Capacity: **0.6 Kt/y**
CO_2 source: DAC
Year: **2022**

Company: **Celanese, USA**
Capacity: **80 Kt/y**
CO_2 source: **recycled**
Year: **2022**

Celanese

www.methanol.org

Project Overview: e-Methanol number of steps

Existing plants: 2-step e-Methanol

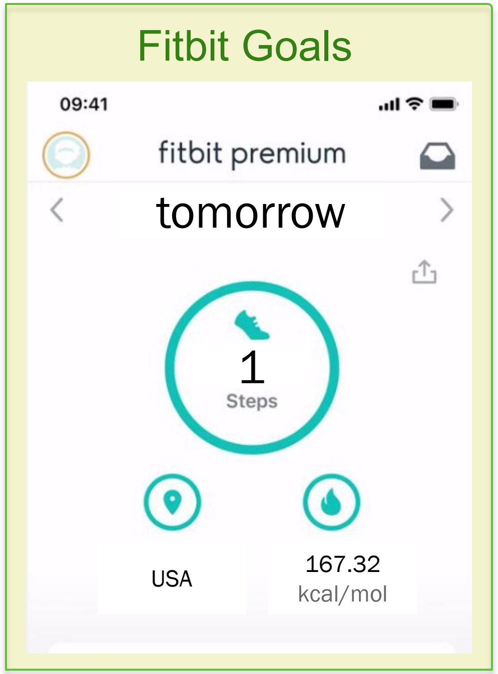
$$3H_2O \xrightarrow{\text{e-chem}} 3H_2 + 3/2O_2$$

$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O$$

E-chem is easy

Overall setup is more complicated

More energy used



Our approach: 1-step e-Methanol

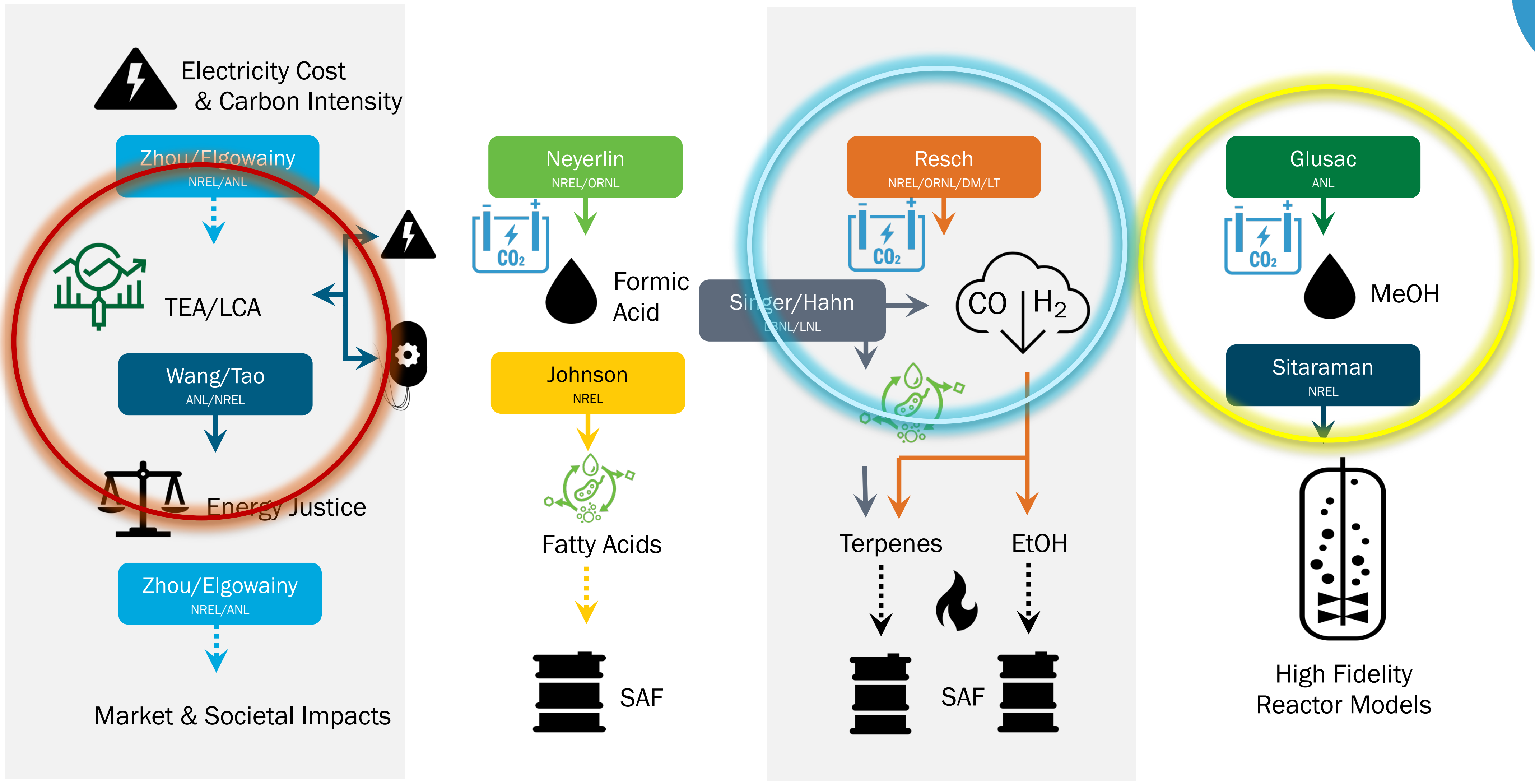
$$CO_2 + 2H_2O \xrightarrow{\text{e-chem}} CH_3OH + 3/2O_2$$

Simpler, all in one step

Less energy used

E-chem more challenging

Project Overview: Connection with Consortium



Project Overview: Connection with Consortium

TEA Analysis of two-step and one-step e-methanol production:

Existing plants: 2-step e-Methanol

$3H_2O \xrightarrow{\text{e-chem}} 3H_2 + 3/2O_2$

$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O$

Energy Efficiency= 64%

CO_2 → MeOH synthesis → MeOH

H_2 ↑

MSP:
$6.45/GGE

Electricity cost: $0.068/kWh; H_2 cost: $4.5/kg

Our approach: 1-step e-Methanol

$CO_2 + 2H_2O \xrightarrow{\text{e-chem}} CH_3OH + 3/2O_2$

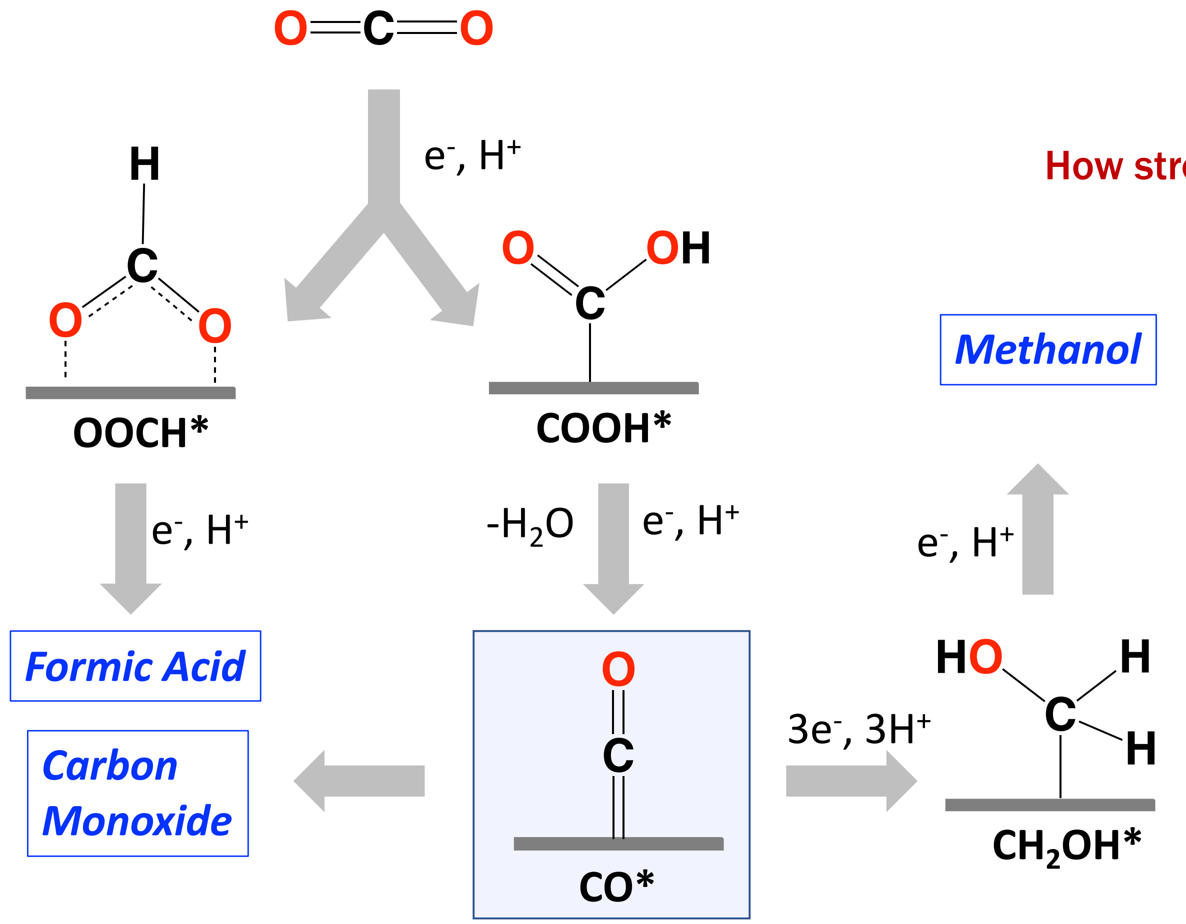
Work in progress.

Ling Tao
(NREL)

Jenny Huang
(NREL)

Goal: to identify what electrolyzer performance we need to achieve to make a single-step methanol generation economically competitive with a two-step process.

Approach: Theoretical Background



How strongly should CO bind to the electrode?

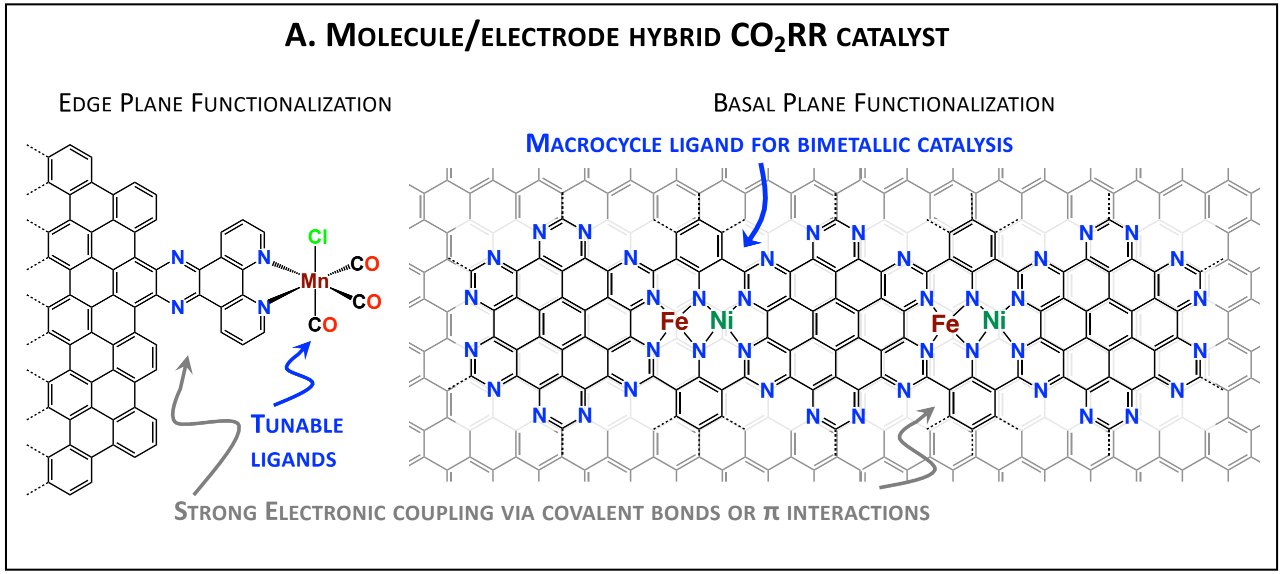
Too weakly: CO formation

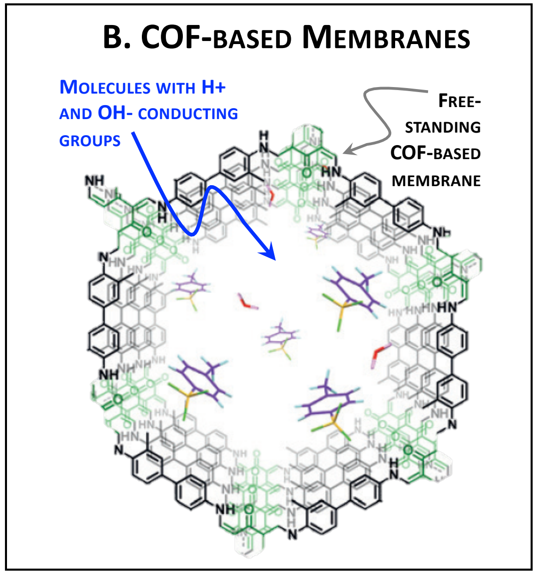
Too strongly: electrode poisoning

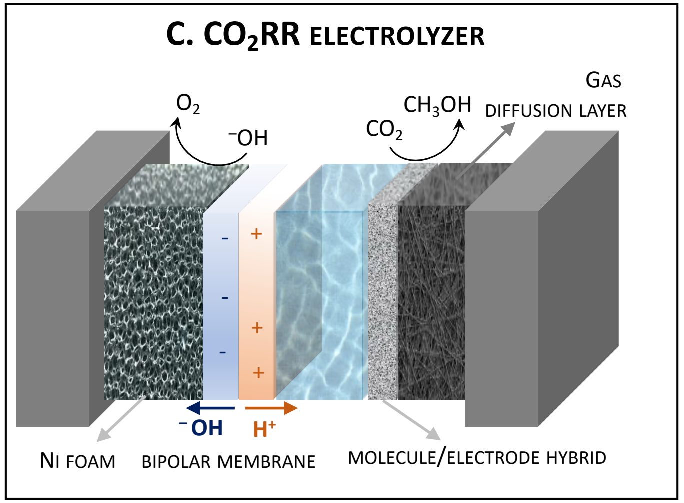
Just right: CH_3OH formation

Progress and Perspectives of Electrochemical CO_2 Reduction on Copper in Aqueous Electrolyte
Chemical Reviews **2019** *119* (12), 7610-7672; DOI: 10.1021/acs.chemrev.8b00705

Approach: Tasks







- **Task 1.** Carbon electrode functionalization with molecular catalysts (Glusac, Myers, Zapol).
- **Task 2.** COF-based membranes for H+/OH- conduction and prevention of methanol crossover (Glusac, Smith).
- **Task 3.** CO2R electrolyzer coupled with anodic water oxidation (Smith).

Approach: Tasks

Project Milestones:

Jan 1 2022

12/31/2022

5 cm^2 electrolyzer
>50 mA/cm^2
20% FE

6/30/2023

Go-No Go: BPM
potential <1.2 V
current >100 mA/cm^2

9/30/2023

5 cm^2 electrolyzer
>50 mA/cm^2
40% FE

Sep 30 2024

25 cm^2 electrolyzer
>200 mA/cm^2
60% FE

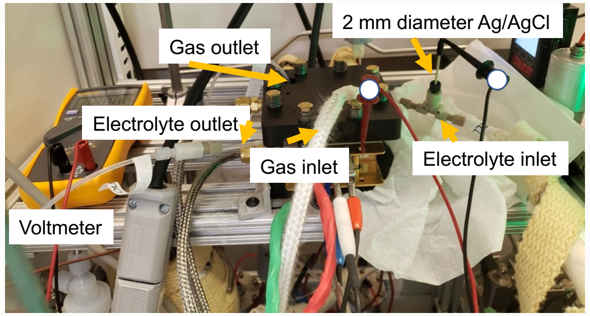
Milestone Name/Description	End Date	Type
Task 2: COF-based bipolar membrane work: demonstration of the reverse-bias water dissociation transmembrane potential of <1.2 V at current densities >100 mA/cm^2 (ANL/NREL)	12/31/2022	Quarterly Progress Measure
Task 1: Finish the computational screening of bimetallic catalysts. Calculate energy landscape for CO_2 reduction to C1 products (CH_3OH, CO, HCOOH) for at least 15 homonuclear and heterodinuclear complexes (ANL).	03/31/2023	Quarterly Progress Measure
Task 1: Successful synthesis and characterization of at least 3 new electrode materials. The Co-based transition metal complexes will be made and attached to the carbon electrodes. Each electrode material will be made on the 100 mg scale.	06/30/2023	Quarterly Progress Measure
Task 3: Finish CO2R electrolyzer testing using Co-complex/CNT cathode catalyst, a commercial BPM, and a NiFe-based anode catalyst. Target performance: 5 cm^2 electrolyzer operating at up to 50 mA/cm2 with >40% methanol Faradaic efficiency (ANL and NREL).	9/30/2023	Annual SMART Milestone
COF-based BPM work: reverse-bias water dissociation transmembrane potential <1.2 V at current densities >100 mA/cm^2. No Go pivot: stop exploring bipolar membranes and focus on cathode materials.	6/30/2023	Go/No Go
25 cm^2 electrolyzer operating at >200 mA/cm^2 for at least 100 hrs while maintaining methanol selectivity of 60% Faradaic efficiency.	12/31/2024	End of Project Milestone

Approach: Experimental Details

3-ELECTRODE MEASUREMENTS

Only the cathodic process monitored.
Electrode area: 0.5 cm^2
Controlled potential electrolysis
Product detection measured at each potential.
Faradaic efficiency determined from the charge that passes through.

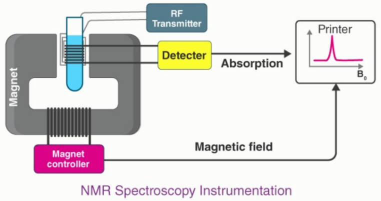
CO_2 ELECTROLYZER



- Both cathodic and anodic (O_2 evolution) processes monitored.
- Electrode area: several cm^2
- Controlled current electrolysis

Product detection:

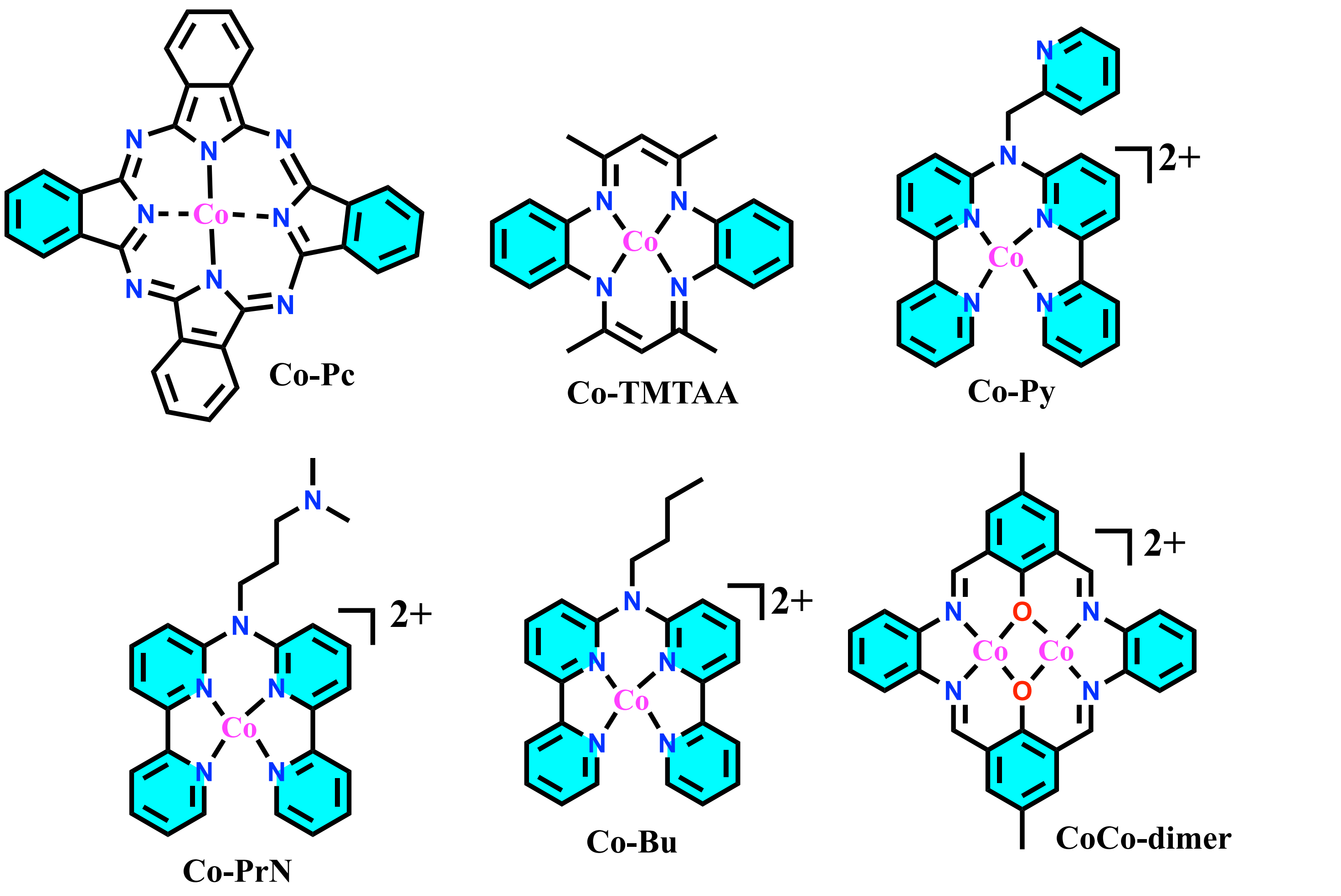
GC for volatile products: CO and H_2



NMR for liquid products: CH_3OH

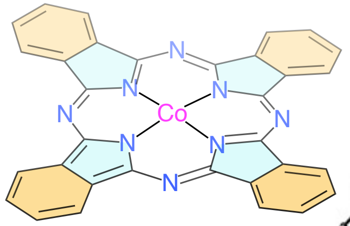
Progress and Outcomes: Task 1

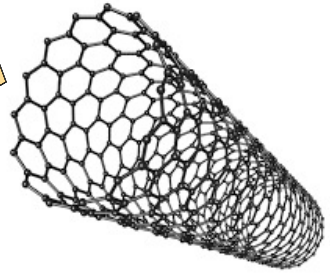
New Co-macrocycles synthesized:



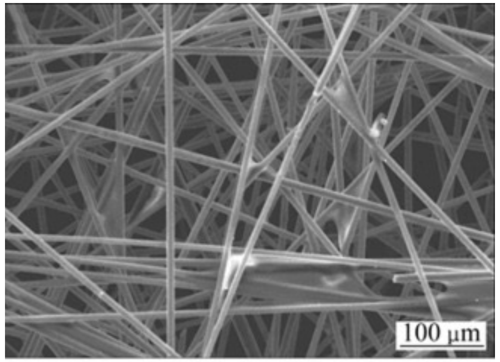
Sreenivasulu Chinnabattigalla (Glusac)

Progress and Outcomes: Task 1



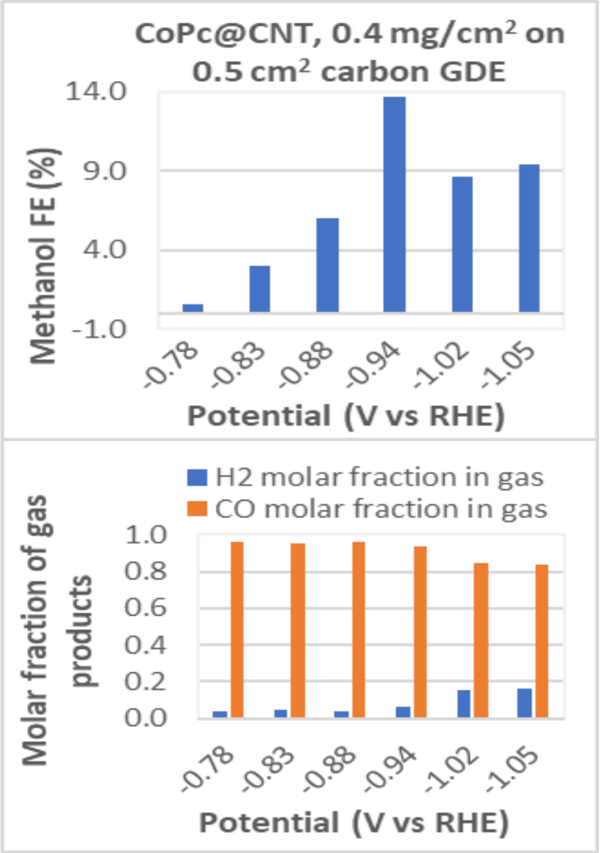


CNT



CF

Molecular catalyst immobilized on the carbon electrode: CH_3OH formation observed.

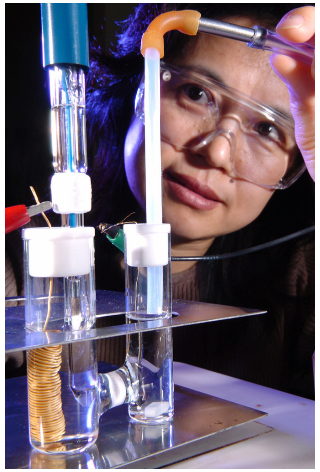


3-electrode test:

14% CH_3OH FE at -0.94 V vs RHE

(44% is the literature report)

Alice Zheng
(Glusac)



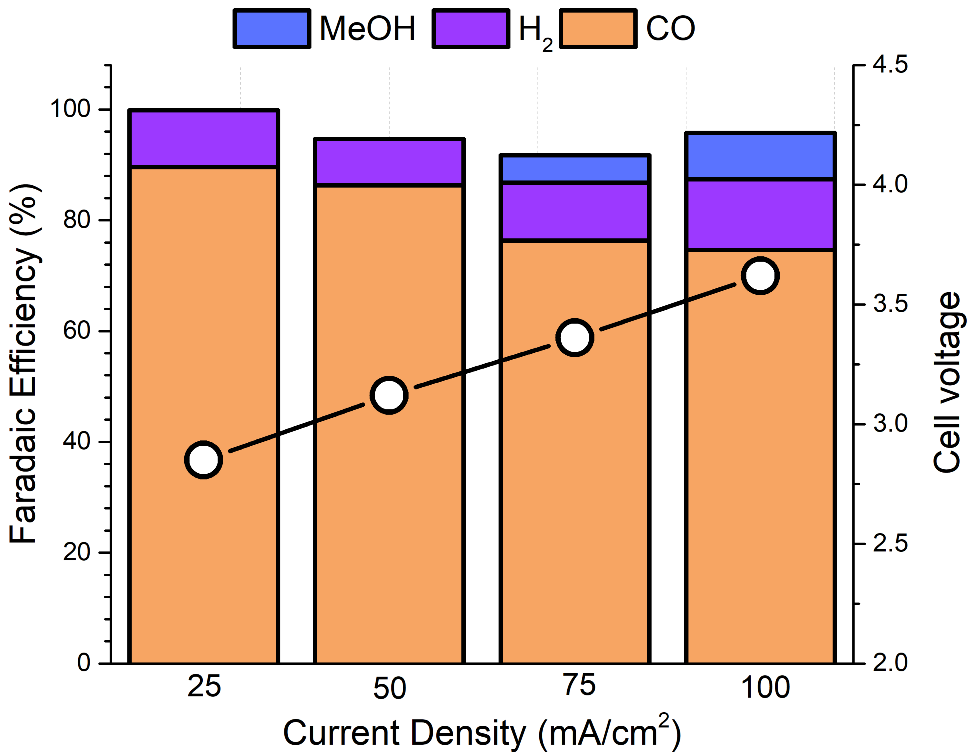
Xiaoping Wang
(Myers)

H. Wang, Nature 2019, https://doi.org/10.1038/s41586-019-1760-8

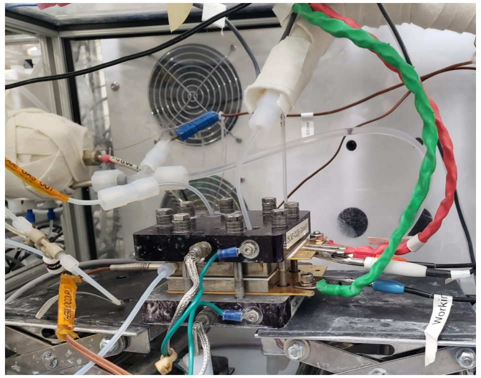
Progress and Outcomes: Task 3

At low current densities, CO formation with high FEs.
As the current density increases, MeOH formation observed ($\sim$10% FE at 100 mA/cm^2).

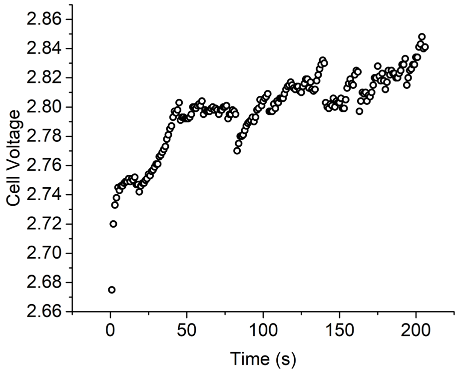
Danielle Henckel (Smith)



A)



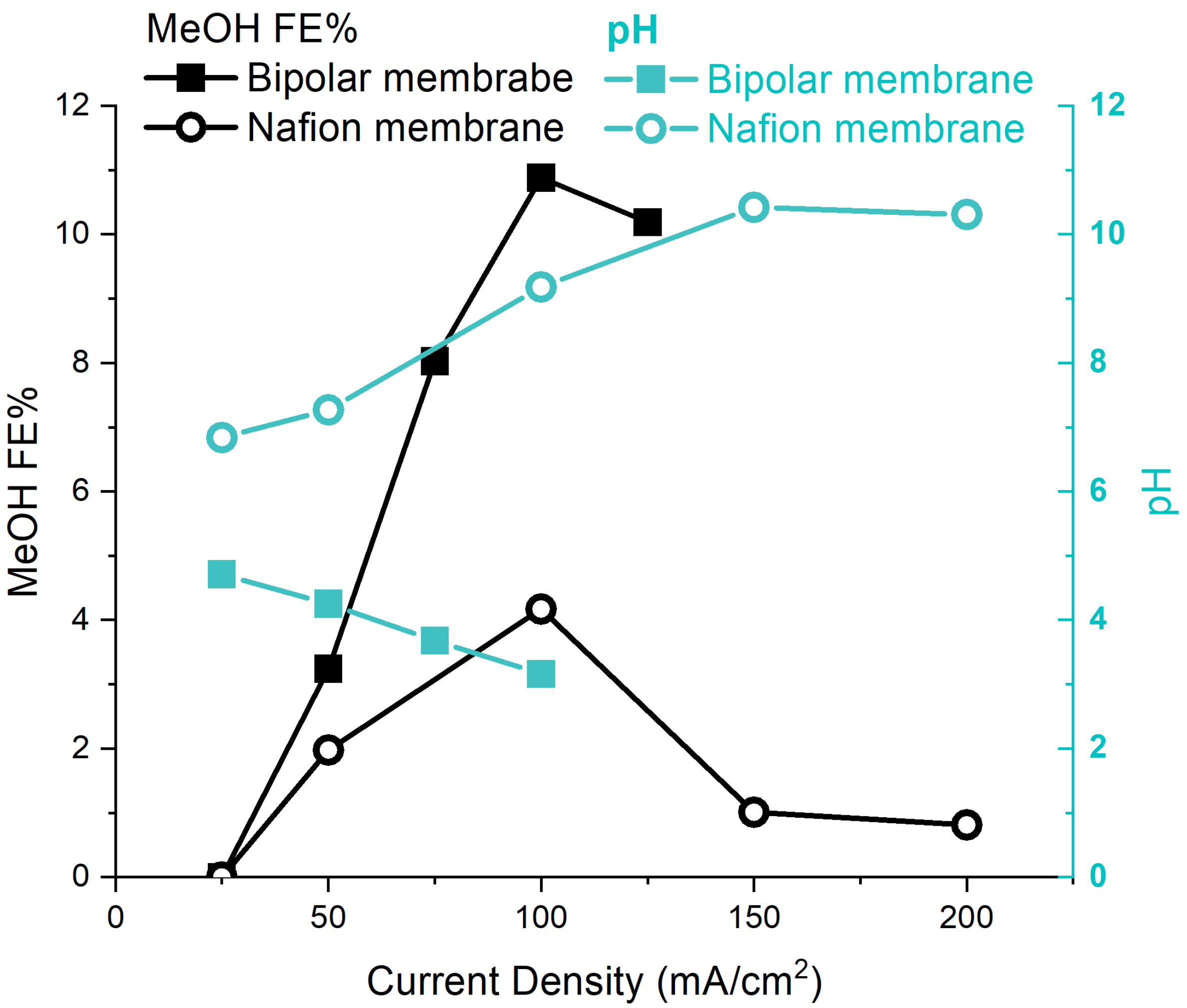
B)



CO_2 electrolyzer
Cathode: 1.1 mg/cm^2 CoPc/CNT/CF on GDE; **Anode:** Ni-foam
Membrane: Fumasep BPM
Catholyte: 0.4 M K_2SO_4
Anolyte: 1 M KOH
Conditions: 60 °C, 95% RH, 1 SPLM CO_2

Progress and Outcomes: Task 3

The pH of the electrolyte makes a big difference:



Danielle Henckel (Smith)

Lower the pH, higher the MeOH yield!

Impact

- Materials for CO_2 to CH_3OH electrolyzers
- Co-macrocycle/carbon electrode hybrid catalysts
- 11% CH_3OH Faradaic efficiency achieved
- ~80% CO Faradaic efficiency achieved
- Collaboration with Ling Tao on TEA analysis

Thank You

DOE – Kevin Craig
Ian Rowe
Robert Natelson

ANL - Michael Wang
Amgad Elgowainy

LLNL - Chris Hahn

LBNL - Steve Singer
Eric Sundstrom

NREL - Michael G Resch
Ella Zhou
Hariswaran Sitaraman
Wei Xiong
Jack Ferrell
Gary Grim
Ling Tao
K.C. Neyerlin
Chris Johnson
Kimmy Mazza
Amie Sluiter